

## THE DB5 CAPILLARY COLUMN : THE SEARCH FOR SENSITIVITY

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### ABSTRACT

Pattern recognition is a useful tool in the identification of point source emissions of PCDFs and PCDDs. Various gas chromatographic conditions have been published for the separation of PCDDs and PCDFs on a DB5 capillary column (2-4), but no account has been made to their relative efficiencies of separation or detection limit (sensitivities).

### INTRODUCTION

The need for routine and accurate monitoring for low levels of congeners of PCDFs and PCDDs has increased due to environmental exposure from hazardous waste sites and combustion sources. Total group analysis can therefore be of use in two areas.

1. To assess the health risk from an environmental incident by determining the congener concentrations.
2. To construct PCDF and PCDD congener profiles for use in identifying pollution sources.

Although PCDFs and PCDDs can be classified into eight groups according to their chlorine content, only those with four or more chlorine atoms attached to the ring structure are used in risk assessment (1). In order to ascertain the congener profiles and their concentrations it is necessary to analyse for every isomer in each homologous group. This is an enormously difficult task requiring both high resolution chromatography to separate the isomers and high selectivity and sensitivity to detect the PCDFs and PCDDs at very low concentrations. In order to maintain this sensitivity the following points must be taken into consideration.

1. When using high resolution gas chromatography the area of a peak remains constant for a given concentration of an analyte. The peak width at half height is typically three to four seconds.
2. For increased sensitivity the mass spectrometer should operate in selected ion monitoring (SIM) mode, monitoring the two most abundant ions in the mass spectrum with a minimal decrease in the accelerating voltage.
3. Under ideal conditions there should be approximately ten scans across the eluted peak.

For the complete analysis of all PCDFs and PCDDs containing 4-8 chlorine atoms the minimum number of individual ions to be monitored is 40 (20 ions for the  $^{12}\text{C}$  and 20 ions for the  $^{13}\text{C}$ ).

## RESULTS AND DISCUSSION

In this study the differing conditions reported were evaluated according to the following criteria:-

1. The separation of the groups
2. Peak width at half height
3. The length of time of the analysis

### Group Separation

The integrity of the analysis, especially where recovery standards are used, is best maintained if the whole analysis is performed in one injection. The separation of the groups using the GC conditions described by EPA (2), Wright State University (3) and Kleopfer (4) are expressed in Table 1. In each of the cases there was a sufficient separation of the groups for the complete analysis to be successfully accomplished.

### Peak Area and Sensitivity

Although peak separation is of utmost importance an equally critical consideration is that of peak width as this has a direct correlation with sensitivity or limit of detection.

A comparison was made between the peak width of each of the methodologies described and GC conditions where the last eluting TCDF isomer and the first eluting PeCDF isomer elute simultaneously. The results are expressed in Table 2.

TABLE 1.

	Retention Time (mins)					
		<u>Rechem</u>	<u>EPA</u>	<u>Wright</u>	<u>Kleopfer</u>	
					60m	30m
TCDF 1	14:10	20:58	24:50	34:50	24:49	
TCDF 2	17:18	28:40	33:02	39:53	31:28	
PeCDF 1	17:20	29:08	35:50	40:22	31:59	
PeCDF 2	20:37	37:19	43:30	47:13	37:00	
HxCDF 1	21:36	39:22	45:35	49:17	38:25	
HxCDF 2	25:18	43:35	49:45	54:26	42:55	
HpCDF 1	28:05	45:52	51:35	57:25	46:48	
HpCDF 2	31:02	47:47	52:20	59:47	50:14	

The maximum dwell time for the analysis would be 25 milliseconds on each ion including a 10 millisecond settling time between each ion. An associated factor in the analysis of trace levels by voltage SIM is the decrease in sensitivity that accompanies the corresponding decrease in accelerating voltage. On magnetic sector mass spectrometers this voltage scan imposes a restriction not encountered on quadrupole instruments, namely that the highest  $m/z$  monitored must be less than about 1.67 times the lowest  $m/z$  monitored (i.e. within the mass range 300-500). It is clear that in the case of the PCDFs and PCDDs the mass range is well within the range specified but the decrease in sensitivity is significant at trace levels to render the analysis impractical.

The maximum sensitivity of the mass spectrometer will be maintained if the decrease in accelerating voltage is kept to a minimum during the SIM voltage scan i.e. the PCDFs and PCDDs are analysed in groups according to their chlorine content.

#### EXPERIMENTAL

A DB5 capillary window defining mixture containing the first and last eluting isomers was obtained from Promochem, St Albans, UK. The experiments were performed on a VG 70S double focusing high resolution mass spectrometer equipped with a Hewlett Packard HP5890 gas chromatograph operating at 10,000 resolution, 30eV and 500 A trap current.

The gas chromatographic conditions investigated by ourselves and other investigators were:

	<u>Rechem</u>	<u>EPA</u>	<u>Wright</u>	<u>Kleopfer</u>
Inj temp	280	280	280	280
Gas	HELIUM at 1-2 ml/min			
GC Interface	330	330	330	330
Temperature 1 ( $^{\circ}$ C)	130	200	190	90
Time 1 (mins)	2	2	2	5
Rate 1 ( $^{\circ}$ C/min)	20	5	5	25
Temperature 2 ( $^{\circ}$ C)	270	220	220	200
Time 2 (mins)	10	16	16	15
Rate 2 ( $^{\circ}$ C/min)	1	5	5	4
Temperature 3 ( $^{\circ}$ C)	286	235	235	250
Time 3 (mins)	5	7	7	10
Rate 3 ( $^{\circ}$ C/min)	0	5	5	4
Temperature 4 ( $^{\circ}$ C)	0	330	330	330
Time 4 (mins)	0	5	5	5

TABLE 2.

TCDF peak width at half ht (secs)	Peak Height of GC eluted Peaks on 60m DB5			
	<u>Rechem</u>	<u>EPA</u>	<u>Wright</u>	<u>Kleopfer</u>
	3	8	10	6
Peak ht normalised relative to Rechem	100	37	30	50

The results indicate that the GC conditions described by Kleopfer will give the greatest sensitivity for the TCDF isomers. A vast improvement in sensitivity can be obtained under the 'Rechem GC' conditions. The major drawback with this protocol is that a complete separation of the last TCDF and first PeCDF is not achieved but in most environmental samples analysed by Rechem the 1289-TCDF is not present so this should not cause undue concern in the majority of cases.

In 1987 the EPA (2) recommended the use of  $^{13}\text{C}$  labelled 1289-TCDF and  $^{13}\text{C}$  1346E-PeCDF as retention markers, if these were used in the analysis then retention time shifts when using the Rechem Protocol would be evident.

### CONCLUSIONS

Although many groups have published gas chromatographic conditions for the analysis of the PCDDs and PCDFs, it is important to utilize those methodologies that improve sensitivity. The results expressed in this study clearly indicate that by employing the gas chromatographic conditions proposed by Rechem, and careful consideration of the type of sample, a great improvement in sensitivity can be achieved.

The conditions proposed by Kleopfer et al indicate that a lower boiling point solvent may be used, possibly aiding in the increased solubility of the PCDDs and PCDFs especially of the OCDD.

### REFERENCES

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